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## THE ABSTRACTION OF OXYGEN FROM THE ATMOSPHERE BY IRON<sup>1</sup>

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That the affinity between oxygen and iron has been the chief factor in the concentration of the latter into workable deposits is one of the most generally recognized facts of chemical geology, although our knowledge of the details of the various reactions involved is far from complete. Indeed, there are few occurrences of iron ores in regard to whose precise method of formation there is not much diversity of opinion.

With ore deposits and with the details of genetic processes, the present paper is not concerned, its aim being to consider one broad result brought about by the chemical relations of oxygen and iron.

The question at issue is: Has there been a progressive oxidation of iron since the beginning of geologic time, involving the abstraction of oxygen from the atmosphere?

Several questions are suggested by the consideration of the main topic, but at present they can hardly be touched upon. Indeed, it is with considerable hesitation that the main theme is here presented, since the data for its thorough consideration are not yet available. But even if the conclusions reached must be regarded as to a high

<sup>1</sup> This paper was written in 1903, in the course of a general consideration of the circulation of mineral matter, and was laid aside for subsequent revision and elaboration, with the hope that further data might be obtainable.

The discussion of the same theme by President C. R. Van Hise (*A Treatise on Metamorphism*, Monograph XLVII, U. S. Geological Survey, pp. 950, 951) has suggested the publication of the paper, in spite of its lack of completeness, since the subject treated is of such a nature that a comparison of independently deduced figures, even though quite divergent, may be of value; and since, moreover, in spite of such divergence of numerical results, the final conclusion as to the importance of the problem presented is the same in both cases.

President Van Hise has been so kind as to read the manuscript, and has approved of the publication of its contents, for which courtesy the writer takes this opportunity of expressing his sincere thanks.

degree tentative, it is hoped that the mere formulation of the problem may be sufficiently suggestive to prove of some value.

Under atmospheric conditions, with abundant oxygen, iron is stable in the ferric condition, and during the circulation of mineral matter involved in the processes of denudation and sedimentation there would be, in the absence of opposing agents, a strong tendency toward the conversion of ferrous into ferric compounds, resulting, in the case of thoroughly disintegrated and decomposed materials, in a complete oxidation of the iron. The younger sediments, in so far as they are derived from other sediments, implying a thorough working over of their materials, would contain little or no ferrous iron. But opposed to this process we have the very potent reducing agent, organic matter. Not only does this agent, when present, take up oxygen that might otherwise combine with ferrous compounds, but it is also able to take oxygen from ferric compounds, reducing them to the ferrous state, thus counteracting the tendency toward oxidation above referred to.

According as the one or the other of these processes has predominated during geologic time, there has been a progressive oxidation or reduction of iron, and the rocks of the crust contain more or less ferric iron, while oxygen has been taken from, or added to, the atmosphere. If the processes balance, the ratio between ferrous and ferric iron remains constant, and the atmosphere is unaffected.

It is manifest that a solution of the problem would be afforded by analyses representing, on the one hand, the average composition, so far as ferrous and ferric iron are concerned, of the crust of the earth before denudation and sedimentation began; and, on the other, of the sedimentary rocks.

An approximation to the former is afforded by Dr. F. W. Clarke's<sup>1</sup> estimate of the composition of the "older crust," based upon 880 analyses of crystalline rocks.

For obvious reasons, a reliable estimate of the bulk composition of the sedimentary rocks is much more difficult to obtain, but the figures given by Stoke's analyses<sup>2</sup> are doubtless the best now available, and they are used as the basis of the present discussion. The samples for these analyses were prepared by Mr. G. K. Gilbert, in an effort

<sup>1</sup> *Bulletin No. 168*, U. S. Geological Survey, p. 14.      <sup>2</sup> *Ibid.*, p. 17.

to get results that might represent the average composition of the sedimentary rocks, and there can be no doubt that the figures give a much closer approximation to the truth than would be afforded by a larger number of analyses taken at random. There is the further advantage that the analytical work is thoroughly reliable—a matter of first importance, and particularly so when it is a question of ferrous and ferric iron.

As in the analyses of limestones, the iron is all given as ferric oxide, the figures are not available for the present inquiry, but the iron content of these rocks is too small to be of great moment. An effort has been made to get from other sources evidence as to whether the correction for limestone would be plus or minus, but as most analyses combine the ferrous and ferric iron, and often the alumina as well, no definite conclusion was reached.

Not only does the small amount of iron in limestones affect the magnitude of this correction, but it is further reduced by the fact that the limestones are of minor moment in the mass of sediments. Gilbert<sup>1</sup> estimates the limestones as making up one-fifth of the total thickness of the sedimentary rocks. Reade's<sup>2</sup> estimate is one-tenth. Therefore, in view of the small percentage of iron in the limestones and their limited amount, they may be neglected without seriously affecting the results.

A more important question is that of the relative masses of shales and sandstones, and the consequent values to be attached to the figures for these rocks. No entirely satisfactory data are at hand to determine this point, but Gilbert's<sup>3</sup> estimate of equal parts of shale and sandstone is here used as being the best available.

As pointed out below, a change of this ratio would affect the magnitude, but not the sign, of the results. In the following estimates, therefore, the figures for shale and sandstone are given equal weight.

According to Clarke's estimate, the older crust of the earth contains 2.63 per cent.  $\text{Fe}_2\text{O}_3$  and 3.52 per cent.  $\text{FeO}$ . The analyses of Gilbert's samples, by Stokes, give for shales<sup>4</sup> 4.03 per cent.  $\text{Fe}_2\text{O}_3$  and 2.46 per cent.  $\text{FeO}$ . For sandstones<sup>5</sup> the figures are 1.24 per

<sup>1</sup> *American Geologist*, March, 1894, p. 214.

<sup>2</sup> *Chemical Denudation in Relation to Geological Time*, 1879, p. 53.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Op. cit.*, p. 17, column C.

<sup>5</sup> *Ibid.*, column F.

cent.  $\text{Fe}_2\text{O}_3$  and 0.57 per cent.  $\text{FeO}$ . These figures represent the results as stated in five distinct columns, in each of which the direction of the change is the same—an increase of the ratio of ferric to ferrous oxide as compared with the corresponding ratio in the old crust.

By combining the figures for shales and sandstones, we have, as an expression of the iron contents of the sedimentary rocks, excluding limestones, 2.64 per cent.  $\text{Fe}_2\text{O}_3$  and 1.52 per cent.  $\text{FeO}$ .

Comparing these figures with those given above for the older crust, the contrast is pronounced. In the older crust the ferrous oxide is in excess, while in the sediments the ferric oxide is markedly preponderant. This relation is expressed by the following ratios:

In older crust,  $\text{FeO}:\text{Fe}_2\text{O}_3::3.52:2.63$ , or about 1:0.75.

In sediments,  $\text{FeO}:\text{Fe}_2\text{O}_3::1.52:2.64$ , or about 1:1.75.

In other words, in the old crust there is about three-fourths as much ferric as ferrous oxide, while in the sediments there is about one and three-fourths times as much.

Corresponding ratios for the two chief groups of sediments are as follows:

Shales,  $\text{FeO}:\text{Fe}_2\text{O}_3::2.46:4.03$ , or about 1:1.64.

Sandstones,  $\text{FeO}:\text{Fe}_2\text{O}_3::0.57:1.24$ , or about 1:2.17.

Thus, as stated above, the magnitude, but not the sign, of the results for the sediments will vary with the weights given to shales and to sandstones. But even were the figures for shales taken alone, throwing out the sandstones entirely, it is evident that the ratio of ferric to ferrous oxide is double that found in the older crust.

As the shales, sandstones, and limestones represent, in altered form, the materials of the old crust, and as the two latter show, as compared with the old crust, a decrease of iron, while the shale shows no increase, it is clear that, if the analyses are to be used as a basis of calculation, allowance must be made for concentration of iron in ores and other highly ferruginous rocks. Moreover, in the change from old crust to silicious sediments, there must be a loss of calcium and magnesium to form limestones, and of sodium held in sea-water, while there is a gain of carbon dioxide and water.

In view of these facts, it is probable that 4 per cent. is a moderate estimate of the total oxidized iron of sediments, excluding limestones, and it is assumed that the ratio between ferrous and ferric oxides is that above derived from Stokes's analyses.

To determine the amount of oxygen combined with iron in the sediments, Joly's<sup>1</sup> estimate of the mass of silicious sediments,  $64 \times 10^6$  tons (of 2,240 pounds) is taken as the amount of shales, sandstones, and ferruginous rocks.

This gives  $256 \times 10^{14}$  tons of iron, which, occurring as  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  in the ratio 2.64:1.52, requires  $96 \times 10^{14}$  tons of oxygen. The same amount of iron occurring as  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$  in the ratio of the old crust, 2.63:3.52, requires  $8,765 \times 10^{12}$  tons of oxygen.

The difference between these two amounts,  $835 \times 10^{12}$  tons, is a measure of the quantity of oxygen taken from the atmosphere and fixed in the silicious sedimentary rocks through the agency of iron. Calculating, from Woodward's<sup>2</sup> statement as to the mass of the atmosphere, the total amount of oxygen as  $1,213 \times 10^{12}$  tons, the quantity abstracted by iron is equal to 68.8 per cent. of that now present in the atmosphere.

While this estimate manifestly can lay no claim to even approximate accuracy, it suffices to show that the abstraction of oxygen by iron is a factor that cannot be disregarded in any attempt to work out the geological history of the atmosphere.

<sup>1</sup> *Scientific Transactions of the Royal Dublin Society*, Vol. VII, Ser. II, p. 46.

<sup>2</sup> *Bulletin No. 78*, U. S. Geological Survey, p. 34.